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Specific Heats of Tars

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BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

H. M. CHILES

ENTITLED..... SPECIFIC HEAT OF TARS.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF..... BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING.

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Specific Heats of Tars.

In recent years the importance of tars and tar products has increased greatly due to a number of causes. The growing demand for coke especially for metallurgical purposes has brought about the development of important industries for the utilization of the by-products tars, gas etc.

Until the present war the advancement in this line in this country had been slow as is shown by comparing the number of by-product coking plants with those of the old bee hive type. But the war has brought about the realization that our industries must be made self sustaining and independent of those of those of any other nation. This is especially true of the industries dependent on coal tar products, as this includes the manufacture of dyes and explosives. products which are of the greatest importance in time of war, especially when the war is with the country upon which we had previously been mainly dependent for products of this nature. Consequently there has been a very rapid development along these lines in this country since the beginning of the present war. This development is quickly noticed by comparing the per cent of the total coke manufactured in by-product coking plants now with that which was so made before the war.

In spite of the growing importance to our industries of these products very little is at present known about the constituents or properties of the common tars.

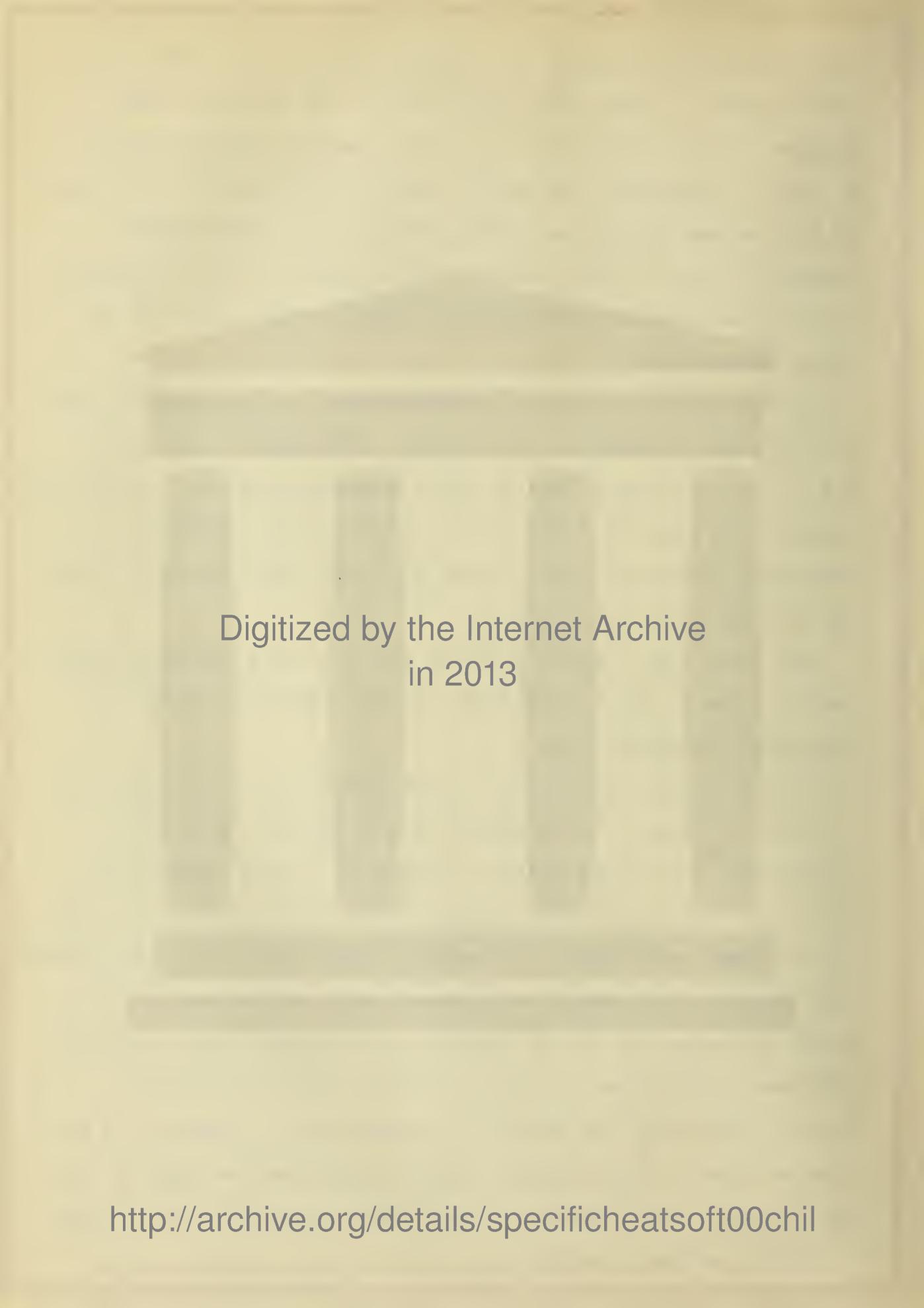
It is quite evident that if the greatest development possible is made further knowledge of the constituents and properties must be gained.

In the handling of tars the common practice is to heat the tar by means of steam coils and pump the tar from the tanks. Further in the distillation of tars a certain definite amount of heat is required to bring the tar up to the distillation point of the various fractions. Consequently in the handling and working of tars it would appear very desirable to know exactly how much heat would be required to bring a given tar up to a given temperature.

For this purpose an exact determination of the specific heat of the common commercial tars and tar fractions is necessary. And up to the present time no exact determinations of the specific heats of tars can be found in the literature, and further the statements which are found are at the best only very approximate and for the most part incorrect.

Tars being very complex mixtures and of a very sticky adhesive nature there is great difficulty in the handling of tars for any exact determinations.

The most common method for the determination of specific heats is that of adding a known weight of the material at a known temperature to a known weight of water at a known temperature and noting the temperature change in the mixture. But tars being nonmiscible with water and forming a mass which does not transfer heat readily this method of mixtures could not be used for any exact determination of its specific heat except under perfectly adiabatic conditions and this condition would be extremely hard to obtain by the method of mixtures with a material of this nature. Some of the existing forms of calorimeters might be used which employ calorimeters of known water equivalent and having a heating medium by which the amount of heat supplied can be

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accurately determined e.g. Electrical heating coils, steam coils etc. But here again the calorimeter must be made adiabatic because of the variance in time necessary to bring the tar and apparatus into temperature equilibrium and further there is considerable difficulty in determining exactly the amount of heat supplied, due to fluctuations in the electric current when comparatively heavy currents are drawn, or to the changes in pressure or quality of the steam. An application of this method has been used * to determine the specific heats of oils, making use of an ordinary fuel calorimeter, by substituting oil for water and using as a material for combustion a pure standard material such as sugar or benzoic acid. While this method has the advantage of availability, there are a number of disadvantages; it requires the use of a very pure material for combustion, if used for other than temperatures near room temperature it requires that the tar be heated before adding to the calorimeter and when making a series of determinations at different temperatures on the same material it requires that the combustion elements be removed after each determination and with heavy viscous materials like tar this would require that the substance whose specific heat was being determined be reweighed after each determination in order to take into account the material removed with the combustion elements and due to the large amount of material used and the long time required to obtain temperature equilibrium with this large amount of a viscous material like tar the calorimeter must be made adiabatic.

* Gas Chemists Handbook (American Gas Institute)

It was believed that it ought to be possible to eliminate some of the more important of the obvious difficulties and errors of these methods.

EXPERIMENTAL:-

In making a calorimeter to eliminate the necessity of determining the exact amount of heat supplied, the idea was conceived of using two calorimeters of exactly the same water equivalent and heated by electrical heating coils of exactly the same resistance connected in series, one of the coils being immersed in a known weight of tar and the other in a known weight of water now since the heating coils have the same resistance and are connected in series the current used by each would be the same and consequently the heat produced by each would be the same as that produced by the other and hence the amount of heat supplied would not enter into the calculations. Then neglecting heat losses the specific heats of the tar and water would be in direct proportion to the weights of each used and inversely to the temperature rise produced in the two elements.

The first apparatus constructed was not made adiabatic but the vessels containing the tar and water were placed in Dewar tubes. The vessel and tube for the tar having approximately two and one half times the volume as those for the water. It was thought that in this manner that the heat rise produced on the two sides could be made approximately the same so that the radiation losses would tend to cancel when the comparison was made between the weights of materials in the two vessels and the temperature rise produced.

An idea of the construction and the principles of operation

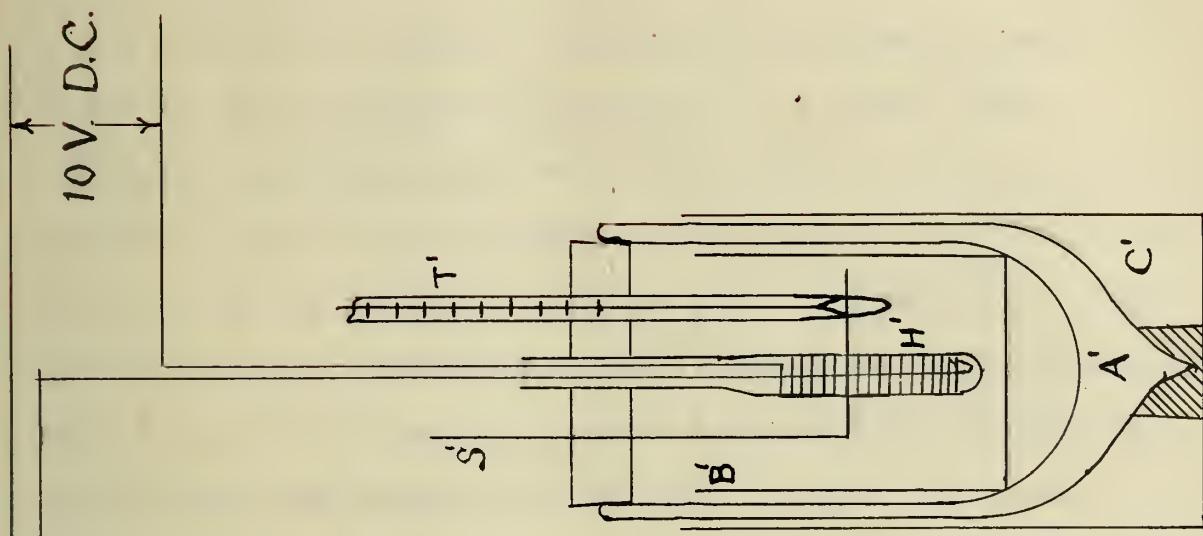
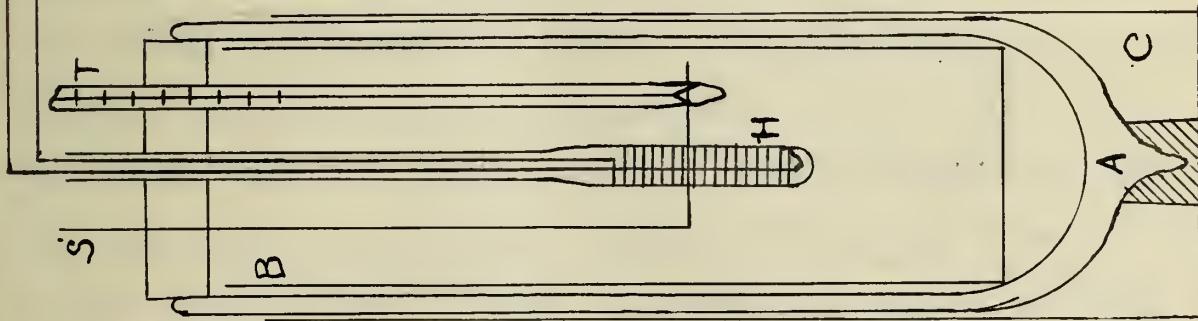
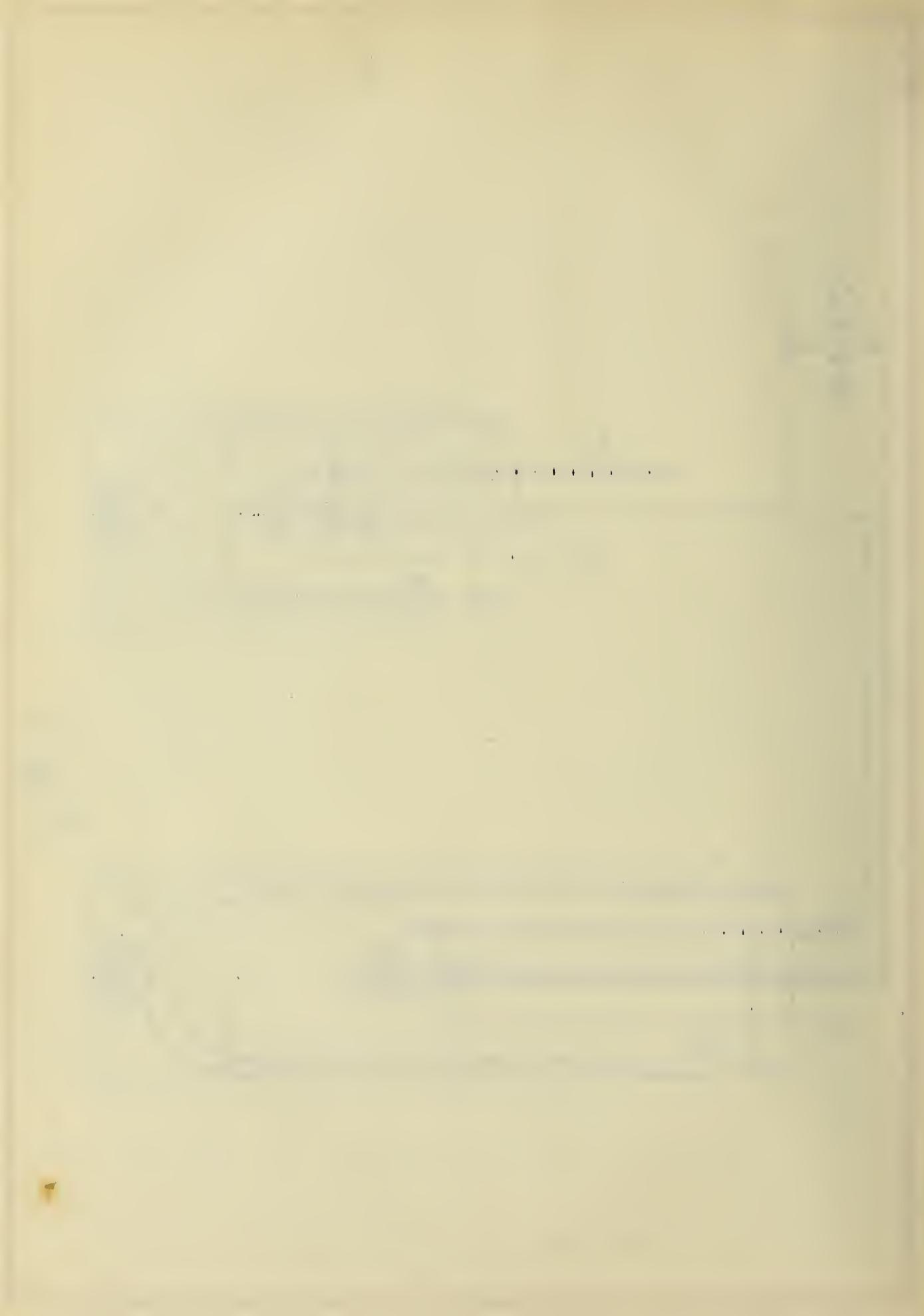


Fig. 1.





Can be gained by referance to the diagram Fig. 1

A and A' are the Dewar tubes ,B and B' are copper vessels for holding the tar and water respectively,H and H' are the glass tubes containing the constantin heating coils the tubes being filled above the level of the coils with trans former oil, S and S' are the stirrers which were operated by hand, C and C' are protective casings for the Dewar tubes.

Trouble was experienced with this apparatus due to the long time required for the tar and apparatus to come to constant temperature ,and before any attempts could be made to get around this difficulty some meddlesome person broke one of the Dewar tubes and as one of the proper size was not available,another calorimeter was designed on the same general principle but being made adiabatic.

In making the second and final calorimeter the two sides were made as exactly duplicate adiabatic calorimeters. For the construction of the seperate units the general plan for the calorimeter Daniels * was followed . In this calorimeter of Daniels' the heating of the adiabatic bath is accomplished by making the calorimeter vessels the electrodes in an alternating current circuit ,the electrolyte which is the liquid in the adiabatic bath is a very dilute solution of copper sulphate. To control the temperature between this adiabatic bath and the inner elements use is made of thermocouples,one junction being immersed in the adiabatic bath and the other in the liquid contained in the calorimeter. The leads from the thermocouples being connected to a sensative galvanometer,by this method Daniels using eight couples was able to keep the temperature

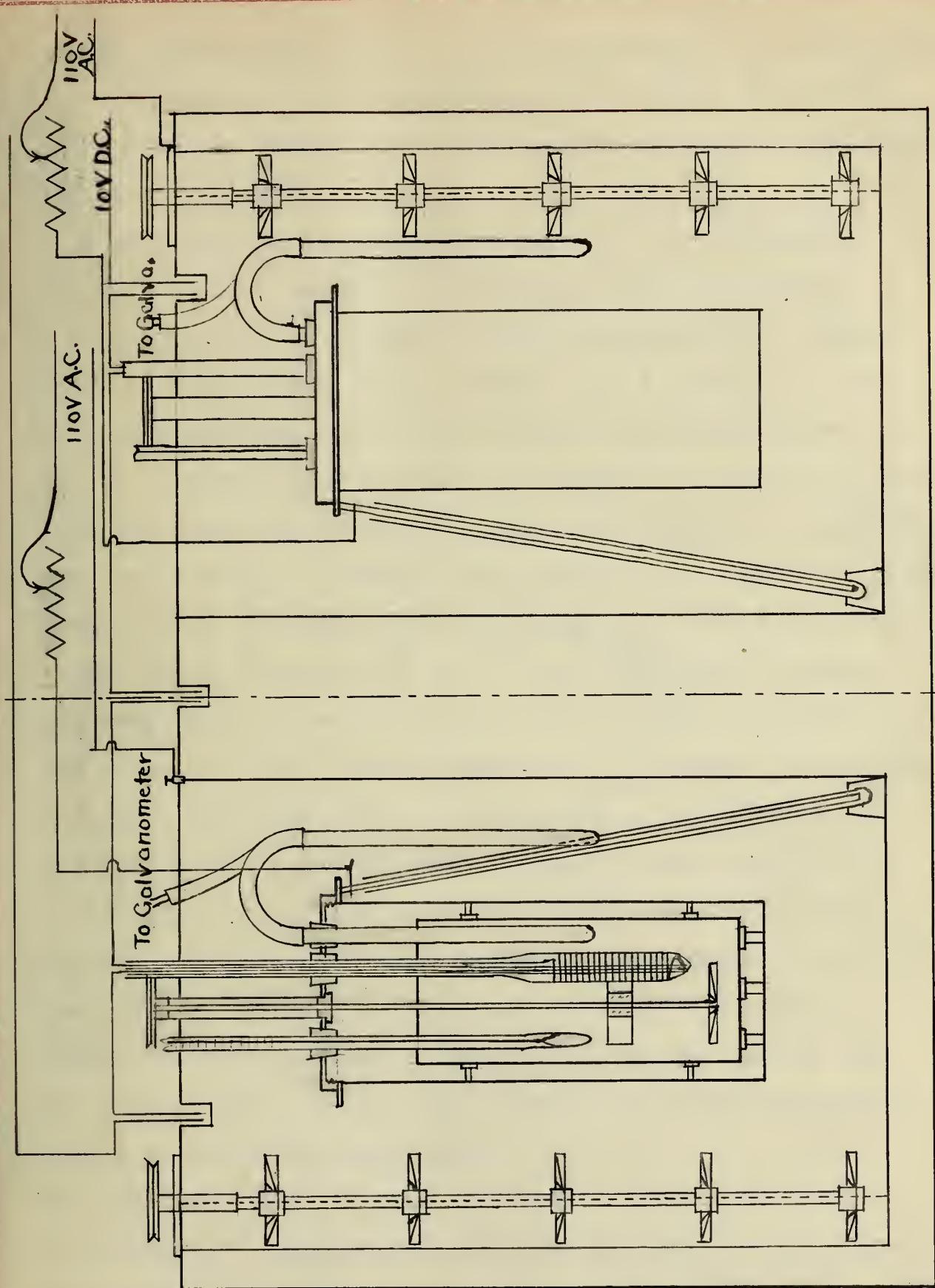


Fig. 2.

jacket always within $.01^{\circ}$ C of the temperature of the calorimeter for a slow rise in the calorimeter, while with a rapid rise of 1.0° C per minute he was able to keep the process adiabatic to within $.02^{\circ}$ - $.03^{\circ}$ C.

A good idea of the general construction and arrangement of the parts can be gained by reference to the diagram Fig. 2 C in the diagram is the inner vessel for holding the material which is being heated, it is a copper can $2\frac{21}{32}$ in. x 6 in. outside dimensions, made from a copper tube with a bottom soldered in. It is held up and away from the vessel B by means of glass rods, the glass rods were fused on to small pieces of constantin wire and the wires soldered to the vessel. The vessel B is made from a piece of heavy brass tubing which is turned down thin except for a distance of $\frac{1}{2}$ in. at one end, a bottom of brass is soldered in the other end and the thick end was threaded to fit the screw cap D, the inside dimensions of this tube are $3\frac{3}{32}$ x 8 inches. The screw cap D is turned from a large brass bar and fitted with a rubber gasket to make a water tight joint. In the top of cap D four holes are bored, into one of these is soldered a piece of brass tubing, in each end of this tube bearings are fitted on which the stirrer rod M turns. Rubber stoppers bearing, a thermometer, the lead in tube for the heating coils and the tube bearing the thermocouples are fitted to the other three holes. The heating coil H is made of constantin wire and has a resistance of approximately $2\frac{1}{3}$ ohm and with the two coils in series on a 10 volt circuit gives a heat rise of approximately 0° C per minute. The lead in wires are made of heavy copper wire and the lead in wire going to the bottom of the coils

is enclosed in a small glass tube.

In order to balance the resistances of the two coils and make their resistances exactly the same the coils after winding and before enclosing in their tubes were connected in series with an ammeter and the lengths of wire in the two coils adjusted until the ammeter gave the same reading for both coils. The two coils were then placed as resistances on the opposite sides of a wheatstone bridge, using a lead storage cell as a source of current and a Leeds and Northup type H mirror scale galvanometer. The sliding contact on the bridge was adjusted to produce a zero deflection of the galvanometer, the positions of the two coils were then reversed and the bridge again adjusted to a zero deflection of the galvanometer. The lengths of wire in the two coils were then adjusted and the process repeated until a zero deflection of the galvanometer was produced with the coils in either position without changing the position of the sliding contact, the slightest movement of the sliding contact in either direction produced a marked deflection of the galvanometer. The two coils were then placed in small test tubes and the leadin wires were enclosed in a glass tube the end of the test tube was then drawn out to the same size as the tube enclosing the lead in wires, the reduced end of the test tube and the end of this tube were then fused together. The remaining space surrounding the coils was then filled with transformer oil, leaving a small air space in the bulb portion of the tube to allow for the expansion of the oil. The resistances of the two coils were then checked against each other by means of the wheatstone bridge as before. The resistances were found to be the same and the coils were ready for use.

The thermocouples T were used to detect any difference in temperature between the adiabatic bath and the calorimeter, they were sensitive enough so that a difference in temperature of $.03^{\circ}\text{C}$ between the two elements could be easily detected when they were connected with a Leeds and Northup type H mirror scale galvanometer. There were sixteen copper-constantin couples with a total length of 14 inches. They were enclosed for a distance of 6 inches from each end in glass tubes sealed at one end. The central part of the couples where they are bent was enclosed in a piece of pure para rubber tubing which fitted over the open ends of the glass tubes enclosing the ends of the thermocouples. The two leads for the thermocouples were brought back inside the glass tubes to the open ends where they were bent back so as to come out between the glass and rubber tubes. The leads were then enclosed in another piece of para tubing and a third piece of tubing stretched over the end of this tube and enclosing as well the end of the glass tubing and the first rubber tube, rubber cement was used in making this joint so that the completed piece was water tight. Before putting the last piece of tubing in place the space inside the tubes surrounding the couples was packed with paraffine wax. The leads from the thermocouples were connected to the galvanometer through a double throw mercury switch so that the same galvanometer could be used for both sides of the calorimeter.

The vessel B is supported by means of an ordinary laboratory tripod the vessel being slipped through the opening in the top and resting on the screw top D, the legs of the tripod are insulated from the can A by means of glass casings which were slipped

over the legs, in the bottom of these casings were placed small wads of cotton to prevent breaking of the glass tubes and to regulate the height of the tripods. Rubber stoppers with holes bored half way through were placed on the bottoms of the glass tubes to prevent breaking and to give a support against the sides of can A which prevented the tendency for the tripod to tip tilt when the stirrer belt was tightened for working with very heavy tars. Various methods were tried for supporting the can B using glass tubes held in place by means of short pieces of brass rod soldered to the sides of the can, but these methods all gave much trouble both through the breaking of the glass tubes and the breaking of the solder holding the brass rods to the sides of the cans.

The outer can A is a galvanized iron can 8 in. x 13 in. with a semicircular compartment on one side so arranged that the stirrers turned half in this compartment and half in the can proper. The entire apparatus was enclosed in a large wooden box 10 in. x 14 in. x 22 in. and the space between this box and the cans was packed with magnesia steam pipe insulation material. The outer bath was heated by means of a 110 volt alternating current one terminal of which was connected to the tripod supporting the can B while the other terminal was connected to the can A. For heating the adiabatic bath on the water side it was found that the ordinary tap water was sufficiently conducting but for the tar side a small amount of zinc sulphate was added to the water to make it a better conductor. In order to regulate the rate of heating a variable resistance was placed in the circuit, this resistance was made of a number of carbon blocks with a screw for adjusting the pressure with which the

blocks were held together .With this resistance it was found possible to so well regulate the rate of heating that it required but little attention .By this means of heating the heat is so well regulated and distributed that vigorous stirring was not necessary, the water was kept circulating by means of a stirrer consisting of four propeller type blades held in place by means of nuts screwed on to the shaft.

All electrical connections were made by means of mercury wells made by boring small holes in the edge of the containing box I and filling these with mercury, this gave not only a very quick method of making connections but gave connections of constant resistance as well . All four of the stirrers of the apparatus were turned by one belt driven by a small D.C. motor.

The thermometers used were graduated into tenths of degrees the maximum range for the one used on the water side was 50° while the one used on the tar side had a maximum range of 102° Both thermometers were compared with a similar thermometer which had been standardized by the U.S. Bureau of standards and corrections curves plotted. The thermometers were always immersed to the same depth so that to save time corrections for emergent stem were calculated for each five degree rise and for emergent stem temperatures of from $21-26^{\circ}\text{C}$ using the formula prescribed on the certificate of the bureau of standards ,curves were plotted for these corrections then these curves were combined with the correction curve as obtained by comparison with the standardized thermometer and all thermometer corrections were taken from these curves.

In weighing out samples the two inner cans which were of the same weight were placed on the opposite pans of an ordinary assaying laboratory balance, approximately 400 g. of water was placed in one of the cans and tar was added to the other until the two nearly balanced water was then added to or subtracted from the water can until there was an exact balance. The inner cans were then put in place and the screw cap bearing the thermometers, heating coils, thermocouples and stirrers was screwed down tightly, the can B and contents were then put in place, all electrical connections were made by means of the mercury wells, the stirrers were then started and the adiabatic bath and the inner elements were brought to the same temperature and the thermometers were read after the temperature had been constant for two minutes. The current was then turned on in the heating coils of the central elements and immediately afterward heat was applied to the adiabatic bath by passing the electric current through the bath acting as an electrolyte as already described. The heat was applied slowly at first and finally regulated so that the heat rise in the adiabatic bath was at the same rate as that in the inner elements and the two were kept as near to the same temperature as possible throughout the run. When ready for taking a reading the current was turned off of the inner heating coils and immediately afterward in the outer bath. It was found necessary however to turn on the current for short periods in the adiabatic bath while the inner elements of the calorimeter are coming to constant temperature, due to the lag in the inner vessel and to the radiation losses from the outer. When the temperatures become nearly constant

care was taken that the adiabatic bath was at a slightly lower temperature than the inner elements so that there will not be a slow rise at the end due to heat exchange after the temperature has been constant for two minutes the temperatures are read. Corrections were made by reference to the correction curves and the specific heat of the material determined by dividing the heat rise on the water side by the heat rise on the tar side and multiplying this result by the specific heat of water at the average temperature over the range through which it was heated.

In making the first test run exactly the same amount (about 400 g.) of water was weighed out into each of the two inner calorimeter tubes the calorimeter was assembled and the test run made with water in both sides of the calorimeter, it was found that the rise on the side to be used regularly for the water was $.02^{\circ}\text{C}$ too great for a total rise of 10°C , due probably to the lighter thermometer used on this side. To correct for this difference the calculated weight of glass necessary was cut from a piece of heavy glass rod and placed in the bottom of the inner calorimeter vessel. The test run then repeated several times when it was found that there was no measurable difference in temperature rise on the two sides for a total rise of 10° .

Test runs were then made on standard materials for which the specific heats were accurately known, such runs were made on benzene, toluene, carbon disulphide and glycerine. The values for the specific heats of these materials were in good agreement with those found in the literature, and the calorimeter was used without further modification for the determination of

the specific heats of samples of various types of commercial tars as well as the heavy fractions of a part of them.

The benzene and toluene used were the purest products of Merck. They were treated with calcium chloride and allowed to stand for twelve hours, then decanted and redistilled, collecting the fractions boiling at 80.0° - 81.0° for benzene and those fractions boiling at 110.0° - 112.0° for toluene. These fractions were then treated with metallic sodium and allowed to stand for twelve hours and redistilled collecting the fractions boiling from 80.0 - 80.5° for benzene, and from 110.7° - 111.2 for toluene. The carbon disulphide and glycerol used were the purest products of Merck but were not further purified. The tars used were all practically anhydrous, all having a water content of less than one per cent.

DATA:-

The specific heats of both the standard materials and the tars and tar fraction were determined at various temperatures duplicate sets of determinations being run in nearly every case. The mean temperature over the range covered in the determination was found and the specific heats found for this range of temperature were plotted at the mean temperature, and a smooth curve drawn through the points plotted.

Specific heats of tars.

No.	Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean corrected temp. for material	Specific heat of material
101	Gas house tar	(a) 29.88 (b) 37.11	(a) 29.88 (b) 37.10	(a) 36.15 (b) 53.73	(a) 36.28 (b) 53.91	45.06	.4084
		(a) 37.11 (b) 43.40	(a) 37.10 (b) 43.41	(a) 53.77 (b) 68.43	(a) 53.91 (b) 68.85	61.38	.421
		(a) 43.40 (b) 49.02	(a) 43.41 (b) 49.02	(a) 68.43 (b) 81.20	(a) 68.95 (b) 81.82	75.54	.4320
101	Gas house tar	(a) 26.31 (b) 32.29	(a) 26.31 (b) 32.29	(a) 28.61 (b) 43.27	(a) 28.61 (b) 43.40	36.00	.4034
		(a) 32.29 (b) 36.66	(a) 32.29 (b) 36.65	(a) 43.27 (b) 53.81	(a) 43.40 (b) 53.99	48.68	.4108
		(a) 36.66 (b) 43.04	(a) 36.65 (b) 43.05	(a) 53.81 (b) 68.72	(a) 53.90 (b) 69.14	61.56	.4214
101	Coke oven tar	(a) 25.90 (b) 30.70	(a) 25.90 (b) 30.70	(a) 27.63 (b) 38.63	(a) 27.63 (b) 33.78	33.21	.4295
		(a) 30.70 (b) 35.30	(a) 30.70 (b) 35.28	(a) 38.63 (b) 49.00	(a) 38.78 (b) 49.13	43.92	.4371
102	Coke oven tar	(a) 25.94 (b) 32.08	(a) 25.94 (b) 32.07	(a) 26.83 (b) 40.91	(a) 26.83 (b) 41.06	33.91	.4300
		(a) 32.08 (b) 41.66	(a) 32.07 (b) 41.67	(a) 40.91 (b) 62.39	(a) 41.06 (b) 62.70	51.88	.4422
		(a) 41.66 (b) 45.74	(a) 41.67 (b) 45.75	(a) 62.39 (b) 71.23	(a) 62.70 (b) 71.79	67.19	.4522

Specific heat of tars

No.	Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean correcte temp. for material	Specific heat of material
103	Water gas tar	(a) 26.02 (b) 30.48	(a) 26.02 (b) 30.48	(a) 28.49 (b) 39.20	(a) 28.49 (b) 39.35	33.92	.4097
"	"	(a) 30.48 (b) 40.70	(a) 30.48 (b) 40.71	(a) 39.20 (b) 63.10	(a) 39.35 (b) 63.42	51.38	.4238
"	"	(a) 46.68 (b) 49.38	(a) 46.69 (b) 49.38	(a) 75.92 (b) 81.88	(a) 76.46 (b) 82.51	79.48	.4434
105	Water gas tar	(a) 26.02 (b) 33.43	(a) 26.02 (b) 33.42	(a) 26.37 (b) 44.27	(a) 26.37 (b) 44.30	35.36	.4105
"	"	(a) 33.43 (b) 42.09	(a) 33.42 (b) 42.10	(a) 44.27 (b) 64.27	(a) 44.35 (b) 64.62	54.49	.4260
"	"	(a) 42.09 (b) 48.28	(a) 42.10 (b) 48.28	(a) 64.27 (b) 78.69	(a) 64.62 (b) 78.66	71.64	.4382
104	Gas house tar	(a) 27.82 (b) 36.99	(a) 27.82 (b) 36.98	(a) 32.12 (b) 54.81	(a) 32.22 (b) 55.01	43.61	.4009
"	"	(a) 36.99 (b) 42.95	(a) 36.98 (b) 42.96	(a) 54.81 (b) 68.91	(a) 55.01 (b) 69.35	62.18	.4149
"	"	(a) 25.45 (b) 36.82	(a) 25.45 (b) 36.81	(a) 24.75 (b) 53.08	(a) 24.75 (b) 53.25	39.00	.3975
"	"	(a) 36.82 (b) 43.03	(a) 36.81 (b) 43.04	(a) 53.08 (b) 67.8	(a) 53.25 (b) 68.2	60.76	.4133
"	"	(a) 43.03 (b) 48.53	(a) 43.04 (b) 48.53	(a) 67.8 (b) 80.48	(a) 68.28 (b) 81.08	74.68	.4254

Specific heats of tar fractions

No.	Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean corrected temp. for material	Specific heat of material
101	Gas house tar fraction above 200°	(a) 26.60 (b) 34.30	(a) 26.60 (b) 34.28	(a) 34.28 (b) 48.13	(a) 34.33 (b) 48.26	41.29	.4066
101	Same	(a) 34.30 (b) 41.10	(a) 34.28 (b) 41.11	(a) 48.13 (b) 64.70	(a) 48.26 (b) 65.05	58.90	.4056
101	Same	(a) 30.80 (b) 34.98	(a) 30.80 (b) 34.96	(a) 43.61 (b) 53.76	(a) 43.74 (b) 53.95	48.84	.4063
101	Coke oven tar fraction above 200°	(a) 34.98 (b) 41.70	(a) 34.96 (b) 41.71	(a) 53.76 (b) 70.11	(a) 53.95 (b) 70.55	62.25	.4054
103		(a) 29.43 (b) 34.35	(a) 29.43 (b) 34.33	(a) 37.28 (b) 48.61	(a) 37.42 (b) 48.74	43.08	.4316
		(a) 34.35 (b) 38.58	(a) 34.32 (b) 38.58	(a) 48.61 (b) 58.29	(a) 48.74 (b) 58.53	53.63	.4329
		(a) 38.58 (b) 43.57	(a) 38.58 (b) 43.57	(a) 58.29 (b) 69.57	(a) 58.53 (b) 70.01	64.27	.4337

Specific heats of tars.

No.	Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean corrected temp. for material	specific heat of material
105	Refined coal tar	(a) 27.03 (b) 35.72	(a) 27.03 (b) 35.70	(a) 31.52 (b) 53.97	(a) 31.54 (b) 54.16	42.85	.3823
		(a) 35.72 (b) 41.72	(a) 35.70 (b) 41.73	(a) 53.97 (b) 69.15	(a) 54.16 (b) 69.58	61.87	.3899
		(a) 41.72 (b) 46.50	(a) 41.73 (b) 46.51	(a) 69.15 (b) 80.50	(a) 69.58 (b) 81.11	75.34	.4134
		(a) 46.50 (b) 49.75	(a) 46.51 (b) 49.75	(a) 80.50 (b) 87.70	(a) 81.11 (b) 88.45	74.78	.4402
105	Refined coal tar	(a) 26.56 (b) 34.45	(a) 26.56 (b) 34.44	(a) 28.62 (b) 49.07	(a) 28.62 (b) 49.20	38.91	.3814
		(a) 34.45 (b) 36.52	(a) 34.44 (b) 36.51	(a) 49.07 (b) 54.23	(a) 49.20 (b) 54.42	51.81	.3847
		(a) 36.52 (b) 42.45	(a) 36.51 (b) 42.46	(a) 54.23 (b) 69.20	(a) 54.42 (b) 69.63	62.02	.3902
		(a) 42.45 (b) 47.06	(a) 42.46 (b) 47.07	(a) 69.20 (b) 80.15	(a) 69.63 (b) 80.75	75.19	.4132
B	Gas house tar	(a) 28.62 (b) 39.70	(a) 28.62 (b) 39.70	(a) 25.90 (b) 52.05	(a) 25.90 (b) 52.21	39.05	.4201
		(a) 39.70 (b) 48.23	(a) 39.70 (b) 48.24	(a) 52.05 (b) 71.02	(a) 52.21 (b) 71.48	61.84	.4419
B	Gas house tar	(a) 37.78 (b) 49.46	(a) 37.78 (b) 49.46	(a) 52.80 (b) 78.52	(a) 52.97 (b) 79.10	66.03	.4462

Specific heats of tars

No.	Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean corrected temp. for material	Specific heat of material
B	Coke oven tar	(a) 27.35 (b) 35.40	(a) 27.35 (b) 35.38	(a) 33.80 (b) 53.25	(a) 33.91 (b) 53.41	43.66	.4107
		(a) 35.40 (b) 43.33	(a) 35.38 (b) 43.34	(a) 53.25 (b) 71.43	(a) 53.41 (b) 71.90	62.65	.4292
		(a) 43.33 (b) 48.22	(a) 43.34 (b) 48.23	(a) 71.43 (b) 82.29	(a) 71.90 (b) 82.92	77.41	.4424
A	Coke oven tar	(a) 27.27 (b) 39.15	(a) 27.27 (b) 39.15	(a) 23.48 (b) 53.20	(a) 23.48 (b) 53.38	38.43	.3962
		(a) 39.15 (b) 46.90	(a) 39.15 (b) 46.91	(a) 53.20 (b) 71.00	(a) 53.38 (b) 71.46	62.42	.4279
A	Coke oven tar	(a) 27.82 (b) 35.44	(a) 27.82 (b) 35.42	(a) 24.42 (b) 43.63	(a) 24.42 (b) 43.76	34.09	.3919
		(a) 35.44 (b) 39.90	(a) 35.42 (b) 39.90	(a) 43.63 (b) 54.51	(a) 43.76 (b) 54.70	49.23	.4083
		(a) 39.90 (b) 46.40	(a) 39.90 (b) 46.41	(a) 54.51 (b) 69.47	(a) 54.70 (b) 69.90	62.30	.4272
C	Water gas tar	(a) 27.83 (b) 39.45	(a) 27.83 (b) 39.45	(a) 29.03 (b) 55.82	(a) 29.03 (b) 56.03	42.53	.4292
		(a) 39.53 (b) 46.65	(a) 39.53 (b) 46.66	(a) 55.45 (b) 70.80	(a) 55.66 (b) 71.26	63.46	.4556
C	Water gas tar	(a) 27.02 (b) 32.26	(a) 27.02 (b) 32.26	(a) 27.43 (b) 39.72	(a) 27.43 (b) 39.88	33.65	.4194
		(a) 32.26 (b) 43.24	(a) 32.26 (b) 43.25	(a) 39.72 (b) 64.37	(a) 39.88 (b) 64.71	52.29	.4415

Specific heats of standard materials

Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean corrected temp. for material	Specific heat of material
Glycerine	(a) 26.72 (b) 34.80	(a) 26.72 (b) 34.78	(a) 25.62 (b) 39.41	(a) 25.62 (b) 39.57	32.58	.5763
Glycerine	(a) 26.91 (b) 35.17	(a) 26.91 (b) 35.15	(a) 26.01 (b) 40.10	(a) 26.01 (b) 40.26	33.15	.5768
CS ₂	(a) 27.01 (b) 29.70	(a) 27.01 (b) 29.71	(a) 25.33 (b) 36.41	(a) 25.33 (b) 36.55	30.94	.2396
"	(a) 29.70 (b) 32.25	(a) 29.71 (b) 32.25	(a) 36.41 (b) 46.89	(a) 36.55 (b) 47.02	41.78	.2429
CS ₂	(a) 26.32 (b) 28.99	(a) 26.32 (b) 28.99	(a) 24.61 (b) 35.59	(a) 24.61 (b) 35.72	30.16	.2396
"	(a) 28.99 (b) 31.39	(a) 28.99 (b) 31.39	(a) 35.59 (b) 45.48	(a) 35.72 (b) 45.61	40.66	.2428

Specific heats of standard materials

Material	Temp. readings for water observed (a) initial (b) final	Temp. readings for water corrected (a) initial (b) final	Temp. readings for material observed (a) initial (b) final	Temp. readings for material corrected (a) initial (b) final	Mean corrected temp. for material	Specific heat of material
Benzene	(a) 26.22 (b) 32.16	(a) 26.22 (b) 32.16	(a) 26.18 (b) 40.11	(a) 26.18 (b) 40.29	33.23	.4198
Benzene	(a) 32.16 (b) 41.23	(a) 32.16 (b) 41.24	(a) 40.11 (b) 60.10	(a) 40.29 (b) 60.56	50.32	.4510
Benzene	(a) 41.23 (b) 46.17	(a) 41.24 (b) 46.18	(a) 60.10 (b) 70.14	(a) 60.36 (b) 70.58	65.47	.4819
Benzene	(a) 26.33 (b) 32.17	(a) 26.53 (b) 32.18	(a) 26.24 (b) 39.96	(a) 26.24 (b) 40.12	33.18	.4203
Benzene	(a) 32.17 (b) 37.51	(a) 32.18 (b) 37.50	(a) 39.96 (b) 52.11	(a) 40.12 (b) 52.27	46.19	.4366
Benzene	(a) 37.51 (b) 50.15	(a) 37.50 (b) 50.15	(a) 52.11 (b) 77.84	(a) 52.27 (b) 78.41	65.34	.4824
Toluene	(a) 26.57 (b) 30.79	(a) 26.57 (b) 30.79	(a) 25.08 (b) 35.08	(a) 25.08 (b) 35.21	30.14	.4156
Toluene	(a) 30.79 (b) 34.98	(a) 30.79 (b) 34.96	(a) 35.08 (b) 44.88	(a) 35.21 (b) 45.01	40.11	.4245
Toluene	(a) 34.98 (b) 44.24	(a) 34.96 (b) 44.25	(a) 44.88 (b) 65.67	(a) 45.01 (b) 66.03	55.52	.4407
Toluene	(a) 26.72 (b) 30.11	(a) 26.72 (b) 30.11	(a) 26.04 (b) 34.09	(a) 26.04 (b) 34.17	30.11	.4158
Toluene	(a) 30.11 (b) 34.41	(a) 30.11 (b) 34.40	(a) 34.09 (b) 44.14	(a) 34.17 (b) 44.27	39.22	.4254
Toluene	(a) 41.34 (b) 48.73	(a) 41.35 (b) 48.73	(a) 52.46 (b) 67.98	(a) 52.63 (b) 68.39	60.51	.4669

Temperature Degrees C.

65

60

55

50

45

40

35

.40

.41

.42

.43

Specific Heat

.45

Water Gas for B

T_{gas}

C.

Gas House for B

T_{gas}

C.

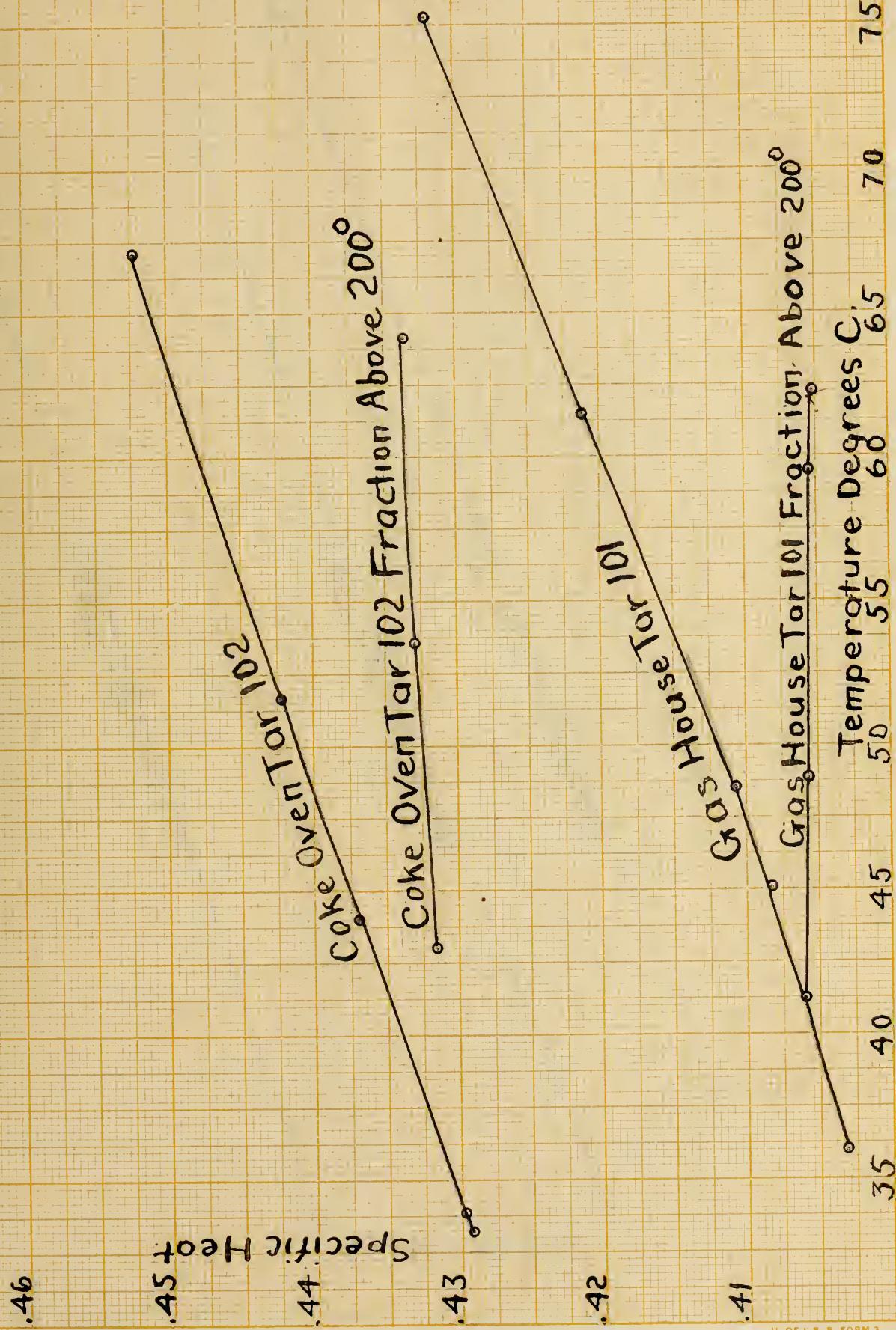
Coke Oven for A

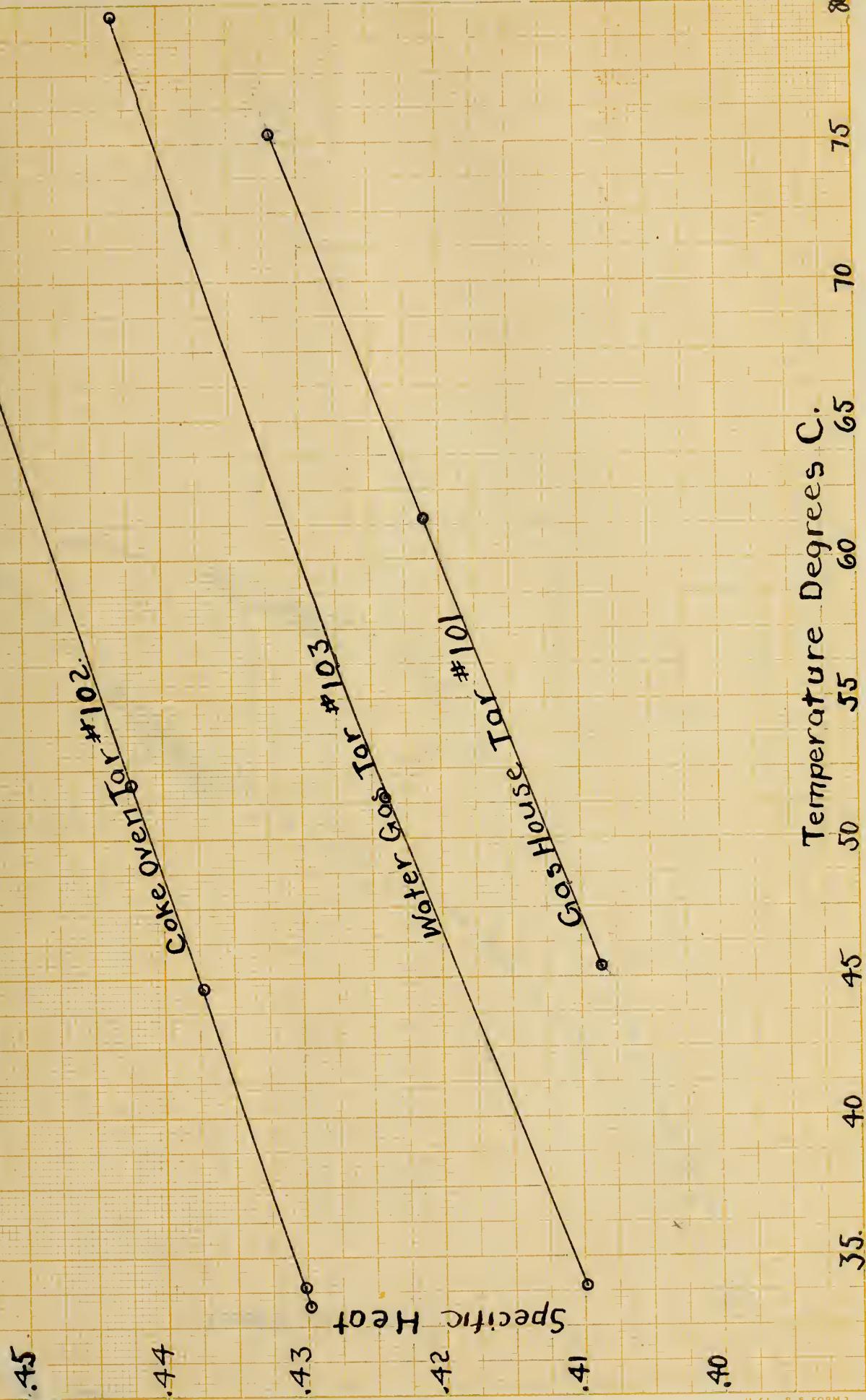
T_{coke}

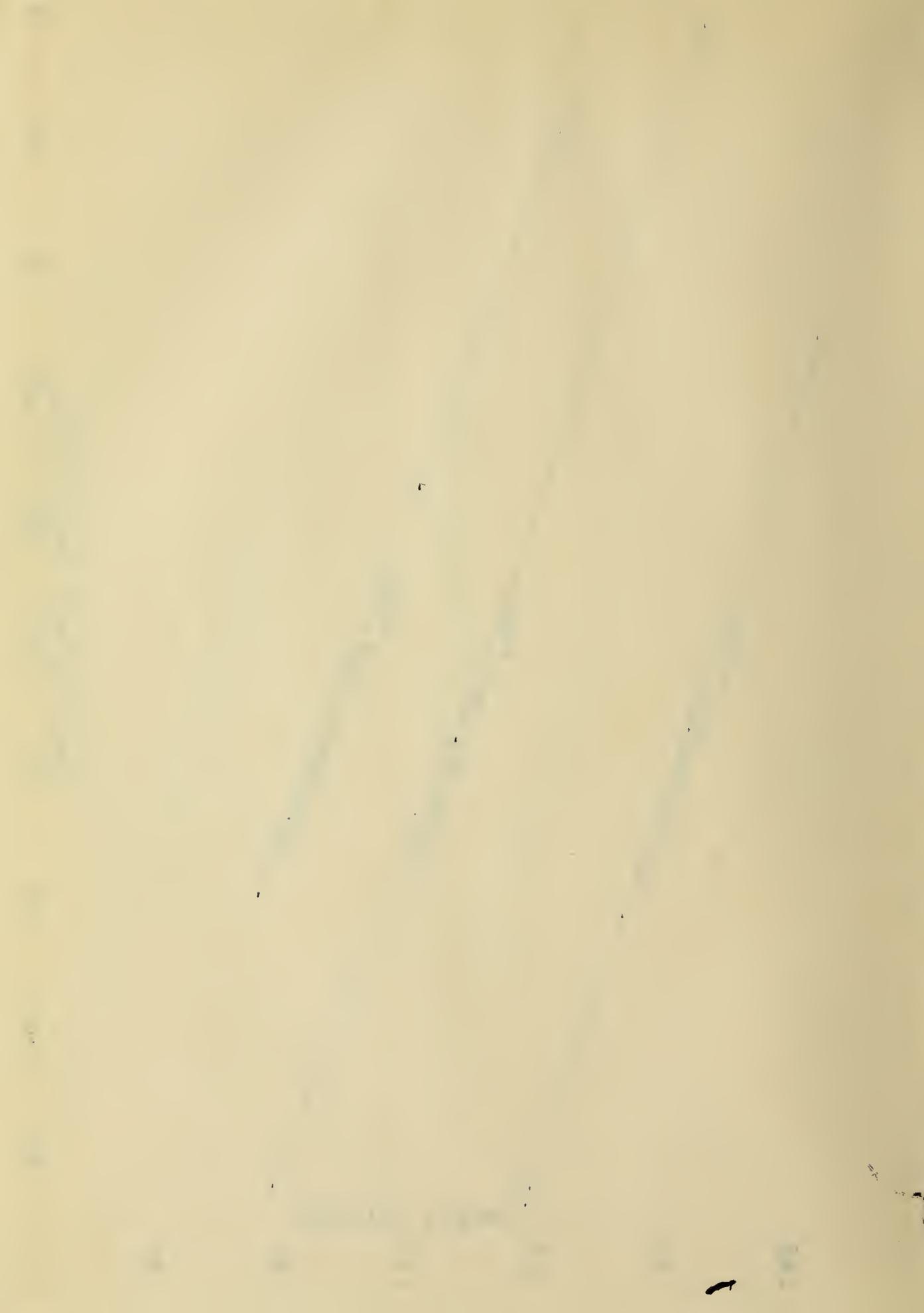
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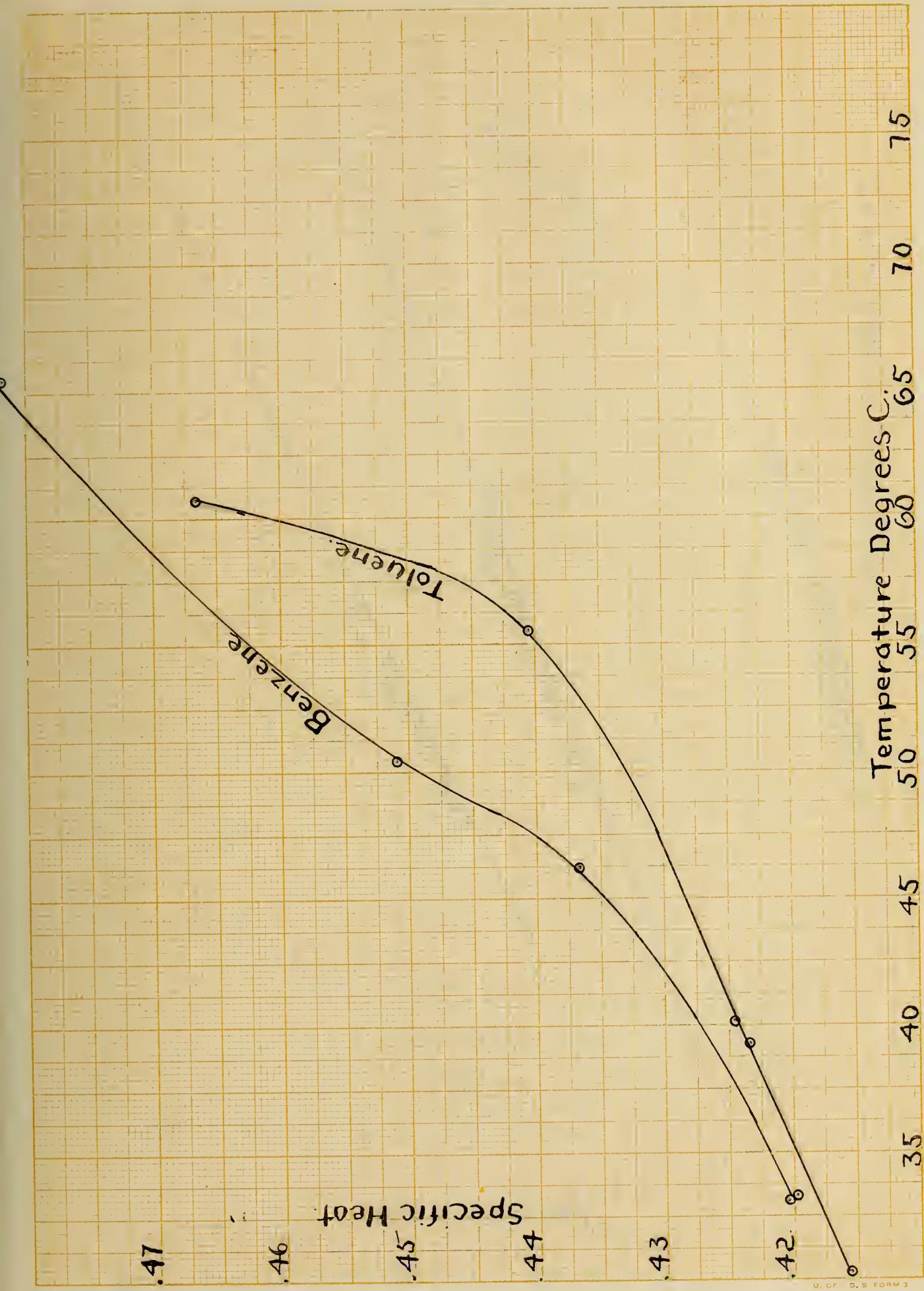
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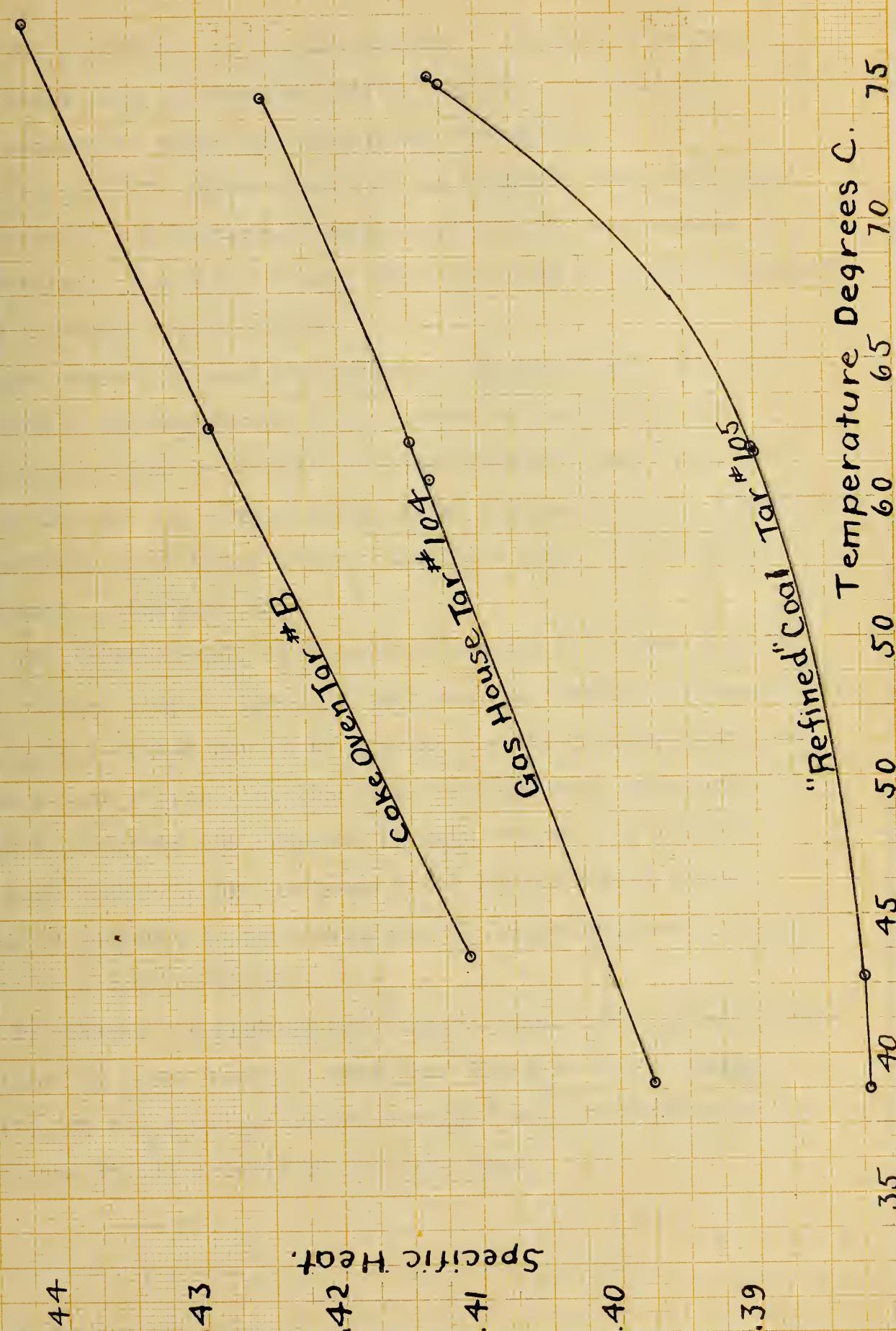
C.











The specific heats of the standard materials show good agreement with the accepted values, which shows well the degree of accuracy of which the calorimeter is capable.

The specific heats of all of the complete tars which were determined all increased rather rapidly with an increase in temperature and for the most part this rise is along a straight line as shown in the curves.

The marked 105 was designated as "Refined" coal tar it appears to be essentially a gas house tar from which the fraction boiling below 170° has been removed. It is peculiar in so far as its specific heat curve follows along an approximate hyperbolic curve, while most of the other tars investigated followed a straight line.

The fraction boiling above 200° of tar 101 shows a small but actual drop in specific heat with an increase in temperature which is peculiar but in as much as the other heavy fractions show a much slower rise than the complete tars, this would tend to indicate the presence in this tar of an abundance of some high boiling substance whose specific heat drops with an increase in temperature, which is present in the other tars to a smaller extent.

In general the heavier and more viscous tars appear to have a slightly lower specific heat than the more fluid ones, while the slope of the curves obtained are approximately the same in all cases of complete tars.

SUMMARY:-

A new form of calorimeter has been devised which makes use of the more important of the recent developments in calorimeter construction. The method of Derby and Daniels for heating the adiabatic bath by making the vessels of the calorimeter itself the electrodes in an alternating current circuit is an especially good method as by this method of heating there is no heat lag and the heat distribution is so good that vigorous stirring is not necessary, in fact for rough work hand stirring would be sufficient or stirring might even be dispensed with entirely.

The employment of thermocouples as used by Dickinson and Daniels for the control of the temperature between the adiabatic bath and the contents of the calorimeter was found to be at once a simple and an accurate method being much easier to manipulate than by the use of two thermometers and in addition can be made as accurate as desired by increasing the number of couples or by using a more sensitive galvanometer or by increasing the distance from the galvanometer to the scale on the galvanometer used.

In addition some novel features not hitherto used employed in calorimetry were used to increase the simplicity and accuracy in making determinations.

The employment of two electrical heating coils of exactly the same electrical resistance connected in series eliminates the necessity of employing constant currents or the measurement of them, and the amount of electricity or the heating value of it does not enter into the calculations, and this fact together

with making the calorimeter adiabatic reduces the calculations necessary for a determination to a minimum.

The specific heats of a number of the more common types and varieties of commercial tars and some of their fractions have been determined with this apparatus. And from these results the following inferences may be made: The specific heats of the common varieties of tars are not widely variant and have an average value at 40.0°C of .4- .43 .

The specific heats of complete tars and their lower boiling fractions increases rather rapidly with an increase in temperature and in most cases rises along a nearly straight line. While the specific heats of the higher boiling fractions is more nearly constant for the range of temperature investigated while the value of their specific heats is slightly lower than that of the complete tar.

The specific heat of a tar does not give a good indication of the character of a tar but in general the heavier and more viscous tars have a slightly lower specific heat than the more fluid tars,

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